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ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor familiar with the calcium carbonate stability determination by analytical measurements of pH and alkalinity and by calculation from temperature, calcium, alkalinity, and residual measurements. Included are objectives, an instructor guide, student handouts, and transparency masters. A video tape is also available from the author. This module considers the mathematical and the analytical determination of calcium carbonate stability, the significance of the test, and application of test results. (Author/BH)

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MARBLE TEST

Training Module 5.235.2.77

Prepared for the

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by

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September, 1977

SE 024 160

Module No:	Module Title: Marble Test
	Submodule Title:
Approx. Time: 2 hours	Topic: Summary

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Calculate the pH of calcium carbonate stability from temperature, calcium level, alkalinity and residue.
2. Experimentally determine pH_s via the marble test.
3. Describe the effects of a pH at, above and below pH_s.

Instructional Aids:

Transparencies Ma1 - Ma3

Surface water videotape

Instructional Approach:

Lecture, discussion, videotape viewing.

References:

1. Operator's manual for pH meter used.
2. Standard Methods for the Examination of Water and Wastewater, 14th edition.

Class Assignments:

Module No:	Module Title: Marble Test
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Effects of pH on Calcium Carbonate

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Write chemical equations describing the dissolution of $CaCO_3$ and the reaction of carbonate ion with H^+ to form HCO_3^-.
2. Write mathematical expression describing the above reactions.
3. Summarize the effects of too high or too low a pH on the dissolution or precipitation of $CaCO_3$.

Instructional Aids:

Transparency MA1: Solubility and acid-base equilibria of $CaCO_3$.

Instructional Approach:

Lecture/discussion

References:

Standard Methods, pp. 61-63.

Class Assignments:

Module No:	Topic:
Ma	Effects of pH on Calcium Carbonate

Instructor Notes:	Instructor Outline:
Transparency Ma-1 Solubility and acid base equilibria of $CaCO_3$	1. Reactions a. solubility $CaCO_3(s) = Ca(aq)^{2+} + CO_3^{2-}(aq)$ b. acid-base $CO_3^{2-} + H^+ = HCO_3^-$ 2. Mathematical Expressions a. $K_{sp} = [Ca^{2+}][CO_3^{2-}]$ b. $K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$ constants are for equilibrium, at equilibrium. c. combining 2a, 2b, at equilibrium (stability) $[H^+] = \frac{K_2}{K_s}[Ca^{2+}][HCO_3^-]$ $pH_s = -\log[Ca^{2+}] - \log[HCO_3^-] - \log[K_2/K_s]$ 3. Effects of pH a. if the pH of the solution is less than pH_s, the solution is unsaturated in $CaCO_3$ and will be corrosive. b. if the pH of the solution is greater than pH_s, the solution is super-saturated with $CaCO_3$ and scale may form.

Module No:	Module Title: Marble Test
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Calculation of pH_s

Instructional Objective:

Upon completion of this module the participant should be able to:

1. From alkalinity, temperature, and filtrable residue, determine parameters needed for the calculation of pH_s.
2. From A, B, $\log[Ca^+]$, $\log(\text{alkalinity})$, calculate the value of pH_s.

Instructional Aids:

Transparency Ma2 - Tables of pH_s parameters.

Instructional Approach:

Lecture/discussion

References:

Standard Methods, p.62.

Class Assignments:

Module No: Ma	Topic: Calculation of pH_s
Instructor Notes:	Instructor Outline:
Transparency Ma-2 Tables of pH_s parameters	1. Use the following data and determinee parameters from tables on transparency a. temperature=20°C, A=2.10 b. residue=200 mg/l, B=9.83 c. Ca^{2+}=100 mg/l, log=2.00 d. alkalinity=50 mg/l, log=1.70 e. have students do likewise with another set of data 2. Show how A, B, log(alk), log$[Ca^{2+}]$ can be substituted: $pH_s=A+B-\log[Ca^{2+}]-\log(alk)$ with example above $pH_s=2.1+9.83-2.0-1.7=8.23$

Module No:	Module Title: Marble Test
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Operation of pH meter.

Instructional Objective:

Upon completion of this module the particpant should be able to:

1. Describe the function of the pH meter.
2. Properly standardize the pH meter.
3. Determine the pH of a solution with a pH meter.

Instructional Aids:

Transparency Ma3 - Diagram of pH meter.

Instructional Approach:

Lecture/ demonstration

References:

Operator's Manual for pH meter used.

Class Assignments:

Module No:	Topic:
Ma	Operation of pH meter

Instructor Notes:	Instructor Outline:
Transparency Ma-3 Diagram of pH meter	1. Demonstrate the parts of the pH meter a. calibration knob b. meter scale c. electrodes 2. Standardize with pH 7 buffer 3. Show how to measure solution pH

Module No:	Module Title: Marble Test
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Experimental determination of pHs.

Instructional Objective:

Upon completion of this module, the participant should be able to:

1. Equilibrate a water sample with $CaCO_3$ marble chips.
2. Measure the pH of the solution which is pH_s.
3. Discuss the advantages of the calculation method and disadvantages of the experimental method.

Instructional Aids:

Surface water videotape

Instructional Approach:

Videotape viewing, laboratory practice

References:

Standard Methods, p.63.

Class Assignments:

Module No: Ma	Topic:

Instructor Notes:	Instructor Outline:
Surface water video tape (last part)	1. Equilibrated sample should be provided equilibration of $CaCO_3$ powder with water as well as the original water sample 2. Measure pH of sample non-equilibrated and equilibrated sample. Determine saturation index=$pH-pH_s$ 3. The experimental method is subject to errors due to the possible absorption of CO_2 from the atmosphere and incomplete equilibration.

Module No:	Module Title: Marble test
	Submodule Title:
Approx. Time: 0.5 hours	Topic: calcium carbonate equilibrium and determination of alkalinity

Instructional Objective:

Upon completion of this module the participant will be able to estimate the calcium carbonate stability of a sample by equilibration and determination of the alkalinity of the calcium carbonate saturated solution.

Instructional Aids:

Instructional Approach:

Laboratory Practice

References:

Class Assignments:

Module No: Ma	Topic: equilibrium determination of alkalinity
Instructor Notes.	Instructor Outline:
see alkalinity module for alkali ity testing and preparation of base.	I. Equilibrate or have available an equilibrated sample of $CaCO_3$ saturated water sample. II. Have students titrate sample before and after saturation with standard base to determine alkalinity of both samples.

Exam Questions

Marble Test
(Calcium Carbonate Stability)

Effects of pH on Calcium Carbonate

1. Will calcium carbonate dissolve at high pH or low pH?

2. The solubility product constant for $CaCO_3$ is the carbonate concentration times the _____ concentration.

3. If the pH of the solution is less/more(choose one) than pH_s the solution is unsaturated in $CaCO_3$ and will be corrosive.

Calculation of pH_s

4. The pH_s of a solution can be calculated from alkalinity, temperature, and _____.

5. The pH_s is equal to the sum of terms A, B, $\log(Ca^{2+})$, and log (_____).

Operation of pH Meter

6. The pH of a solution is equal to negative the base ten log of _____.

7. The buffer solution is used to _____ the pH meter.

8. To determine the pH of a solution immerse the glass _____ and the reference electrode in the solution.

Experimental Defermination of pH_s

9. In the experimental determination of calcium carbonate stability, the solution is equilibrated with what compound?

10. The pH of the equilibrated solution is called _____.

11. Name one disadvantage of the experimental method of determining pH_s.

Exam Questions

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(Calcium Carbonate Stability)

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Operation of pH Meter

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Experimental Defermination of pH_s

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11. Name one disadvantage of the experimental method of determining pH_s.

MARBLE TEST ($CaCO_3$ stability)

EQUIPMENT AND SUPPLIES LIST

1. pH meter
2. pH 7 buffer
3. alkalinity test kit
4. $CaCO_3$ calcium carbonate
5. balance
6. 300 ml BOD bottle
7. filter apparatus

Calcium Carbonate Stability

Laboratory Procedure

I. Calculation Method
   A. For a given water sample, obtain values for temperature, residue, calcium, and alkalinity.
   B. From each of these values determine A, B, log (alk), log $[Ca^{2+}]$ from the tables on transparency Ma2 prepared as a hand-out.
   C. Calculate pH_s for the sample from the formula $pH_s = A+B-\log [Ca^{2+}] - \log$ (alk).
   D. Sample data is included in the data sheet.
   E. Insert calibrated pH electrodes into the water sample. Record pH.
   F. Determine the corrosivity of the sample by subtracting pH_s from pH.

II. Experimental Method
   A. Determine the pH of the water sample by reading the scale of a standardized pH meter.
   B. Determine the alkalinity of the sample by the method used in the "alkalinity" module or by the "test-kit" (Hach) method as follows:
      1. Fill the plastic measuring tube full of sample, pour into mixing bottle.
      2. Add contents of Brom cresol green-Methyl red reagent pillow.
      3. Add dropwize standard sulfuric acid (.03N) solution until color changes from blue-green to pink. Count all drops added.
      4. The total alkalinity is equal to the total drops added times 17.12.
      5. Record total alkalinity and drops acid added to reach end-point.
   C. Add 0.3 grams $CaCO_3$ (calcium carbonate) powder to a 300 ml bottle filled to the top with sample. Replace stopper, being careful to avoid air bubbles - Mix sample every 15 minutes for three hours. Allow sample to stand overnight. Carefully decant 200 ml of the sample without disturbing the sediment. Filter the sample.
   D. Determine the pH (pH_s) and total alkalinity of the sample as in A and B above.
   E. If the original pH is greater than the final pH and if the original alkalinity is greater than the final alkalinity. The sample is super saturated and will deposit a protective coating. If the original pH is less than the final pH and the original alkalinity is less than the final alkalinity, the sample is unsaturated and may be corrosive.
   F. Comment on the corrosivity of the water sample.

B. Sample Titration. Pipet three - 25 ml well mixed sample aliquots into three 125 ml erlynmeyer flasks. Add and mix 25 ml distilled water. Add 1 ml buffer and 2 drops indicator to each flask. Titrate in triplicate with EDTA solution as in A above. Record initial and final buret readings.

III. Calculation and evaluation of results

A. The volume of solution used in each case will be equal to the final minus the initial buret reading. The average volume from the three titrations will be the volume used in calculation. Call this value "A". The total EDTA hardness of the sample is calculated from the formula:

$$\text{EDTA hardness as } CaCO_3 = \frac{AXBX1000}{25} \quad \frac{mg}{l}$$

B. Comment on possible errors, distinctness of end point, and source of sample.

Data Sheet for Calcium Carbonate Stability

Sample number_____

I. Calculation Method

Sample Data

temp 20°C	A =		temp 5°C	A =		Data from Student sample: Temp °C	A=				
Residue 200 mg/l	B =		residue 100 mg/l	B =		resi-due mg/l	B=				
Ca^{2+} 10 mg/l (as $CaCO_3$)	log Ca^{2+}		Ca^{2+} 100 mg/l (as $CaCO_3$)	log Ca^{2+}		Ca^{2+} mg/l (as $CaCO_3$)	log Ca^{2+}				
Alk 10 mg/l as $CaCO_3$	log Alk		Alk 10 mg/l as $CaCO_3$	log Alk		Alk mg/l As $CaCO_3$	log Alk				
	pH_s=			pH_s=			pH_s=				
							pH=				
							pH-pH_s =				

Comment on the tendency of the water to corrode iron pipes or build a protective coating:

II. Experimental Method

A. Original pH_____

Original alkalinity_____mg/l (electrometric)

(test kit) drops H_2SO_4 required_____

alkalinity (drops x 17.12)_____mg/l as $CaCO_3$

B. After $CaCO_3$ equilibration

pH_s_____

alkalinity_____mg/l (electrometric)

(test kit) drops H_2SO_4 required_____

alkalinity (drops x 17.12)_____mg/l

C. Comment on the tendency to form a protective layer or be corrosive:

Analyst_____ Date_____

TRANSPARENCY MAI

Solubility and Acid-base Equilibria of $CaCO_3$

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3 \xrightarrow{\text{heat}} H_2O + CO_2$$

TRANSPARENCY MA2

Tables of pH_s Parameters

Water Temp (°C)	A	dissolved residue (mg/l)	B
0	2.6	0	9.70
4	2.5	100	9.77
8	2.4	200	9.83
12	2.3	400	9.86
16	2.2	800	9.89
20	2.1	1000	9.90

Log table for Ca^{2+} or alkalinity

number	Log	number	Log
10	1.00	200	2.30
20	1.30	300	2.48
30	1.48	400	2.60
40	1.60	500	2.70
50	1.70	600	2.78
60	1.78	700	2.84
70	1.84	800	2.90
80	1.90	900	2.95
100	2.00	1000	3.00

TRANSPARENCY MA3
Diagram of pH meter